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Radiative Exciplexes of 1,2,4,5-Tetracyanobenzene with Sterically Hindered Alkylbenzenes[†]

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The formation of radiative exciplexes of a series of electron donor−acceptor pairs from 1,2,4,5-tetracyanobenzene (**TCB**) and sterically hindered substituted benzenes is reported for the first time. The dependence of radiative and nonradiative electron transfer on the driving force and separation distance in the exciplexes is explored in nonpolar solvents. It is found that exciplexes of donor−acceptor pairs of hindered and unhindered donors with similar structures and electron-transfer properties give almost the same fluorescence quantum yields. Isotope effects of solvents on return electron-transfer rate constants of the exciplexes described above are found to be undetectable. This implies that the exciplexes are approximately two-component systems without the structural involvement of a solvent. Linear relationships between nonradiative return electron-transfer rate constants, log($k_{-\mathrm{et}}$) and the driving force, $-\Delta G_{-\mathrm{et}}°$, are observed for exciplexes from both sterically unhindered and hindered donors. On the basis of all of these results, we conclude that there is no sterically controlled changeover from an inner-sphere to an outer-sphere mechanism in the present systems.

1. Introduction

In liquid solutions, a ground-state donor or acceptor molecule is free to approach an excited acceptor or donor by random walk. After bimolecular charge-transfer quenching of the excited state at the encounter between donor and acceptor, a light-emitting intermediate is sometimes formed.[1,2] This intermediate is usually called an exciplex or excited charge-transfer complex in which the charge and electronic excitation are shared by the donor−acceptor pair. Exciplexes or excited charge-transfer complexes are very important intermediates in the electron-transfer quenching process and many photochemical reactions. Since the pioneering work of Weller and co-workers, much progress has been made toward reaching a general understanding of these intermediates.[1]

However, as far as the general relationship between overall electron-transfer rates and factors that control the formation, structure, and donor−acceptor interaction of the exciplexes is concerned, little detailed knowledge is available. It has been long noted that, when the polarity of the solvents is increased, both the fluorescence quantum yield and decay time of the exciplex decreases, and that the decrease in the fluorescence quantum yield was far greater than that of the decay time.[3,4] In the mechanism proposed by Weller and co-workers,[3] it was assumed that both nonfluorescent ion pairs and fluorescent exciplexes could be formed at the encounters. The fluorescence quantum yield after charge-transfer quenching is determined by both the exciplex formation yield at the encounter and the relative rates of nonradiative and radiative decay in the exciplex. As the solvent polarity is increased, a decrease in exciplex formation occurs because of the formation of solvent-separated ion pairs.

An alternative interpretation was proposed by Mataga et al.[4] In their model, bimolecular quenching reactions at an encounter always result in the formation of an exciplex; the polarity of the solvent will affect the electronic and geometric structure. The exciplex will become more polar with increasing solvent polarity. This will, in turn, decrease the radiative decay rate. Meanwhile, the nonradiative decay rate will increase because of the decreased transition-energy gap between the exciplex and its related Franck−Condon ground state.

To achieve a better understanding of the significance of the above two factors, clear knowledge of the effect of the charge separation distance on rate constants and efficiencies of radiative and nonradiative decay will be a great help. There were earlier studies concerning steric effects in exciplex photophysics. Normally, no emission can be observed when sterically bulky (or bulky) donors or acceptors are used.[5−8] Interestingly, Hubig et al. found, in their recent work, that photoexcited quinones form exciplex-like encounter complexes with aromatic donors that exhibit charge-transfer character.[9] But when sterically hindered donors with similar or identical electron-transfer properties were used, no such encounter complexes were seen.[9,10] The interpretation is that there is a changeover from an inner-sphere to an outer-sphere mechanism in the photoinduced electron transfer. All of these results supported the long-standing point that sandwich π structures with strong charge-transfer interaction are a basic requirement for exciplex formation. To the best of our knowledge, the only exception seen in the literature is that after the quenching of pyrene by 3,5-di-*tert*-butyl-*N*,*N*-dimethylaniline an exciplex with fluorescence emission could be observed.[7,11] But in this exciplex the donor is believed to adopt a pyramidal configuration at the nitrogen atom, which enables it to have a strong localized overlap with the pyrene acceptor molecule.[11]

We report here the first example of exciplex formation between an electron acceptor, tetracyanobenzene, and sterically hindered alkyl-substituted benzene donors. The effects of

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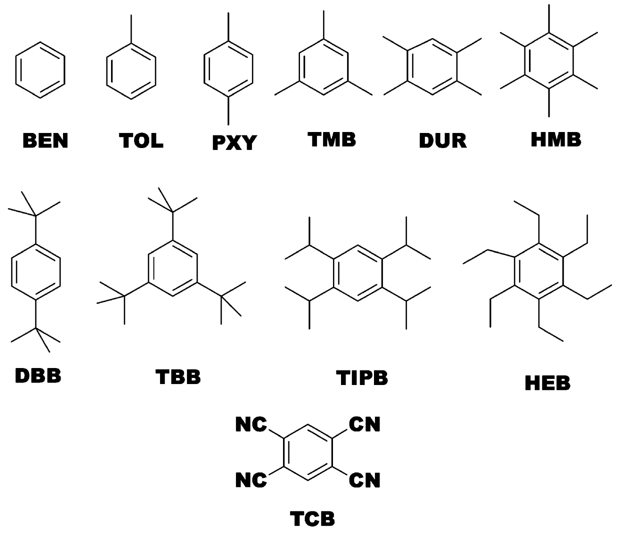
exciplex donor/acceptor separation distance on radiative and nonradiative recombination rates are analyzed.

SCHEME 1



2. Experimental Section

1,2,4,5-Tetracyanobenzene (**TCB**) from Aldrich was used as the acceptor in this work. Donors used were *p*-xylene (**PXY**, Aldrich 99%), 1,4-di-*tert*-butylbenzene (**DBB**, Aldrich 97%), mesitylene (**MS**, Aldrich 99%), 1,3,5-tri-*tert*-butylbenzene (**TBB**, Aldrich 97%), durene (**DUR**, Aldrich, 98%), 1,2,4,5-tetra-*iso*-propylbenzene (**TIPB**, Aldrich, 96%), hexamethylbenzene (**HMB**, Aldrich, 99%), and hexaethylbenzene (**HEB**, Aldrich). Solvents used were benzene (**BEN**, Fisher, 99%), benzene-d_6 (**BEN-d$_6$**, Aldrich, 99%), toluene (**TOL**, Fisher, 99%), Toluene-d_8 (**TOL-d$_8$**, Aldrich, 99%), and 1,1,2,2-tetrachloroethene (**TCE**). The structures of donor and acceptor molecules are shown in Scheme 1.

Fluorescence spectra were recorded using a Perkin Elmer LS 50. Fluorescence lifetimes were measured using time-correlated single-photon counting (single-photon timing). A 355-nm laser pulse from an NV-20001-100 (Uniphase) was used for excitation. The pulses had a duration (fwhm) of 0.8 ns at 13 kHz and an average power of 1 mW. The emission was collected at 90° through a monochromator with a bandwidth of 3 nm located in front of the photomultiplier tube. The output from the laser was focused onto a solution with an absorbance of about 0.1 at 355 nm in a 1-cm cell. Oxygen in the solution was removed by bubbling nitrogen.

3. Results and Discussion

3.1. Emission from Exciplexes Formed between TCB and Sterically Hindered Donors.

TCB is a weak electron-acceptor molecule ($E°_{\mathrm{RED}}$ vs SCE −0.44 V).[12] Electron-donor−electron-acceptor (**EDA**) complexes formed between **TCB** and various electron donors of substituted benzenes have been widely studied for several decades.[13,14]As can be seen from Figure 1, the local absorption band of **TCB** appears below 320 nm in organic solvents such as dichloromethane. In the presence of sterically unhindered (or flat) donor molecules, new absorption bands from **EDA** complexes appear at longer wavelengths. When absorption spectra are recorded in **BEN**, significant spectral overlap between **EDA** complexes of **TCB** with **BEN** and that with the added donor exists. To eliminate the overlap, the absorption spectra of **EDA** complexes of **TCB** with **TOL**, **PXY**, or **MS** are recorded using neat donor **TOL**, **PXY**, or **MS** as the solvent. However, for **EDA** complexes formed between **TCB** and **TOL**, **PXY**, **MS**, or **DUR**, absorption maxima still cannot be directly distinguished. In the present study, the excitation wavelength is fixed at 355 nm, and the excitation directly results in the formation of excited **EDA** complexes. In the nonpolar solvents used, the excited **EDA** complexes thus formed are essentially the same as the exciplexes formed by electron-transfer quenching after the excitation of **TCB**.[12]

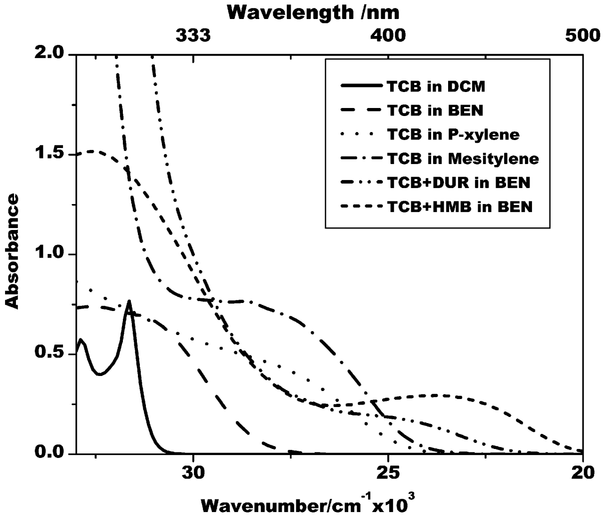
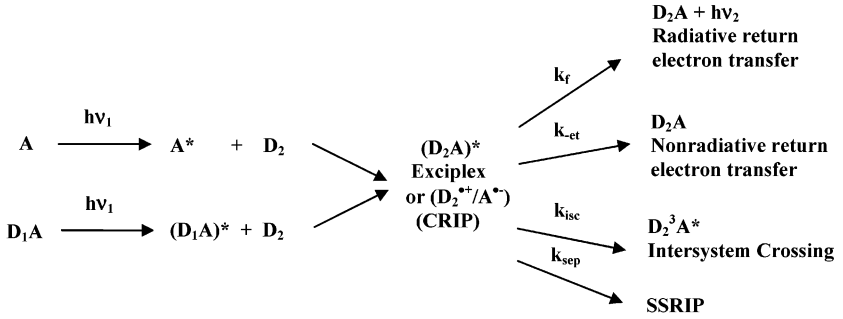


Figure 1. Absorption spectra of 2.5×10^{-5} M **TCB** in dichloromethane, **BEN**, **PXY**, and **MS** and **TCB**'s **EDA** complexes with 0.1 M **DUR**, 0.1 M **HMB** in **BEN**.

In this work, we prefer to use the word exciplex to describe the excited **EDA** complexes formed by both ground-state **EDA** complex excitation and electron-transfer quenching following excitation in local **TCB** bands due to the partial electron-transfer nature of the excited **EDA** complexes in nonpolar solvents. When **BEN** or **TOL** is used as the solvent and a flat molecule such as **PXY**, **MS**, **DUR**, or **HMB** is used as the donor, excitation at 355 nm can result in the direct formation of exciplexes between **TCB** and these donors. It can also result in the formation of exciplexes of **TCB**−**BEN** or **TCB**−**TOL** first, which are then quenched by the added electron-donor molecules to produce exciplexes of **TCB** with these electron donors. The formation and common decay mechanisms for the exciplexes are summarized in Scheme 2. At the donor concentration used (<0.05 M), most of the exciplexes are formed by electron-transfer quenching. As we will discuss later, these exciplexes thus formed can be understood as two-component systems; **BEN** or **TOL** is not actively involved in the exciplex structure but serves simply as the solvent. When bulky molecules such as **DBB**, **TBB**, **TIPB**, and **HEB** are used as the added donors, **EDA**'s absorption of **TCB** with these donors is not detectable at the donor and acceptor concentrations used. Excitation at 355 nm always results in the formation of exciplexes of **TCB** with solvents. The electron-transfer quenching of the exciplexes thus formed produces exciplexes between **TCB** and these bulky donors.

Figure 2 exhibits the steady-state emission spectra of 2.0×10^{-5} M **TCB** with different concentrations of **DUR** in **BEN** after excitation at 355 nm. In the absence of **DUR**, the emission shows the typical broad band of exciplexes of **TCB**−**BEN** with a maximum around 460 nm. When **DUR** is added to the solution, a new emission band with a maximum around 544 nm appears, which corresponds to the emission from the exciplex of **TCB** with **DUR**. To test the effect of steric

SCHEME 2



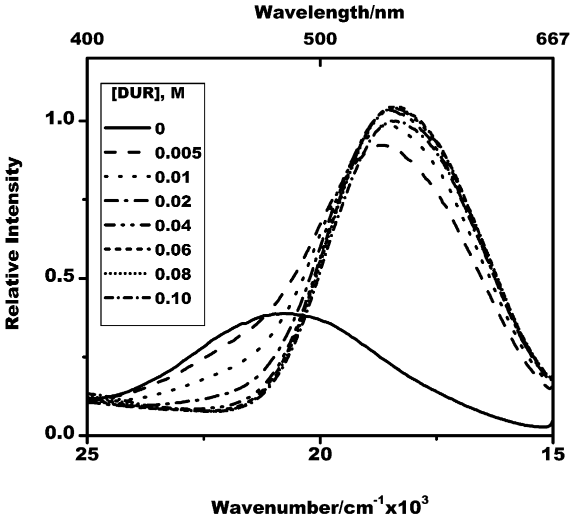


Figure 2. Steady-state fluorescence spectra of 2.5 × 10^{-5} M **TCB** in benzene with different concentrations of **DUR**. Excitation is at 355 nm.

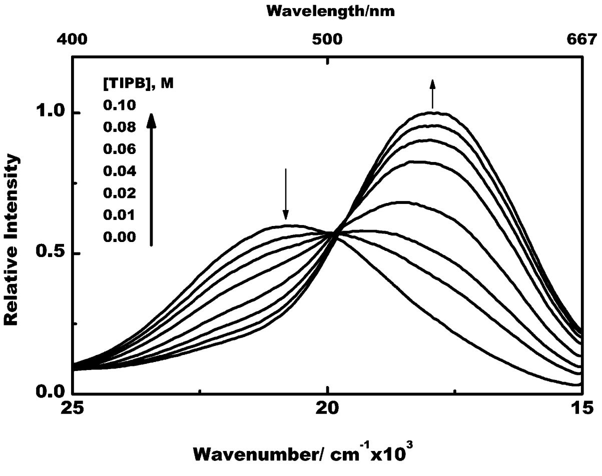


Figure 3. Steady-state fluorescence spectra of 2.5 × 10^{-5} M **TCB** in benzene with different concentrations of **TIPB**. Excitation is at 355 nm.

TABLE 1: Donor Oxidation Potentials, Fluorescence Emission Maxima (λ_{max}^{FL}), Lifetimes of TCB−Alkylbenzene Exciplexes in Different Solvents, and the Relative Emission Efficiencies (I_F^{SH}/I_F^{SUH}) of TCB Exciplexes of Bulky (SH) and Flat (SUH) Donors

donor	solvent	$E_{1/2}^{ox}$ (V)[10,15]	λ_{max}^{FL} (nm)	I_F^{SH}/I_F^{SUH}	τ (ns)
BEN	**BEN**		460		84.0
PXY	**BEN**	2.01	503		36.9
DBB	**BEN**	2.03	506	0.88	122
TMB	**BEN**	2.11	506		46.5
TBB	**BEN**	2.11	507	0.98	72.7
DUR	**BEN**	1.84	544		17.1
TIPB	**BEN**	1.77	554	0.85	33.4
HMB	**BEN**	1.62	578		6.2
HEB	**BEN**	1.59	580	∼1.05	15.2
TOL	**TOL**	2.40	496		73.0
PXY	**TOL**	2.01	504		33.5
DBB	**TOL**	2.03	503	0.90	110.6
TMB	**TOL**	2.11	508		47.2
TBB	**TOL**	2.11	508	0.87	79.5
DUR	**TOL**	1.84	540		19.0
TIPB	**TOL**	1.77	557	0.95	44.5
HMB	**TOL**	1.62	579		7.0
HEB	**TOL**	1.59	580	∼1.05	17.6
PXY	**PXY**	2.01	507		33.8
DUR	**PXY**	1.84			20.7
TIPB	**PXY**	1.77	537	0.92	48.8
PXY	**TCE**	2.01	516		20.7
DUR	**TCE**	1.84			8.3
TIPB	**TCE**	1.77	588		22.2

hindrance on exciplex formation, we used **TIPB**, which has a structure and electron-donation properties similar to those of **DUR** but shows a significant change in steric hindrance because of the four bulky groups on the donor molecule. Figure 3 exhibits the emission spectra of 2.0 × 10^{-5} M **TCB** with different concentrations of **TIPB** in **BEN** after excitation at 355 nm. It is surprising to see that, as the emission from the exciplex of **TCB** with the solvent benzene is quenched by **TIPB**, a new emission band centered at 554 nm appears. This clearly indicates that, accompanying the electron-transfer quenching of the exciplex of **TCB** with **BEN** by the bulky donor **TIPB**, a radiative exciplex between **TCB** and **TIPB** is formed. The reason for the small red shift in the emission maximum of the **TCB−TIPB** exciplex (λ^{em}_{max}: 554 nm) from that of the **TCB−DUR** exciplex (λ^{em}_{max}: 544 nm) might be that **TIPB** (E_{OX}^{O} vs SCE: 1.78 V)[15] is a slightly stronger donor than **DUR** (E_{OX}^{O} vs SCE: 1.84 V).[10] For other bulky donors such as **DBB**, **TBB**, and **HEB**, similar exciplex emissions are observed. The emission maxima of exciplexes formed by **TCB** with the bulky and flat donors discussed above are collected in Table 1. To estimate the steric effect on the emission efficiency of the formed exciplexes, the relative emission intensities of exciplexes from sterically hindered donors compared with those of the corresponding sterically unhindered donors (I_{SH}/I_{SUH}) are calculated and listed in Table 1. The calculations are based on emission intensities of the exciplexes after being normalized to 100% quenching of the fluorescence of the **TCB−BEN** exciplex. Because the changes in the emission spectral shape and the position of exciplexes from bulky donors compared with those of the corresponding flat donors are negligibly small, the relative intensities at the emission maxima are used directly in the calculation without energy correction against the wavelength. Normally, the emission spectra are recorded using solutions with an absorbance of less than 0.1 at 355 nm. To correct for the effect of absorbance differences at excitation wavelengths for

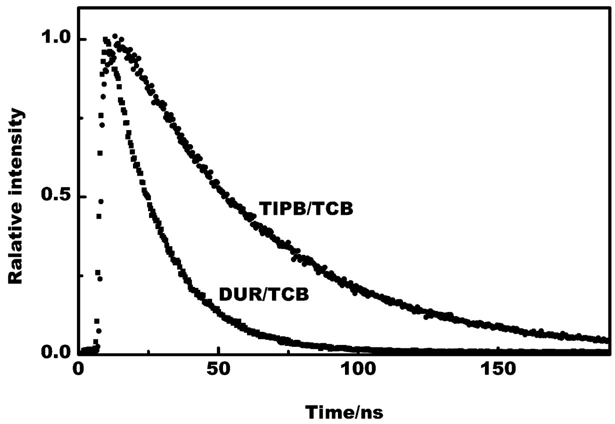


Figure 4. Rise and decay curves of the fluorescence emission of **TCB**−**DUR** and **TCB**−**TIPB** exciplexes in **TOL** after excitation at 355 nm. The emission is monitored at 580 nm.

solutions with bulky and flat donors, ($A_{SUH}I_{SH}/A_{SH}I_{SUH}$) is used to calculate the relative emission intensity, where A_{SUH} and A_{SH} are the absorbance values of the solutions with sterically unhindered and hindered donors, respectively. For most of the donor−acceptor pairs except **TCB**−**TIPB**, the I_{SH}/I_{SUH} values are greater than 0.85. This means that, at least in the nonpolar solvents used, steric hindrance has little effect on the emission efficiency of the formed exciplex. When **TOL**, **PXY**, or **TCE** is used as the solvent, results similar to those in **BEN** are obtained. They are also collected in Table 1. Note that radiative exciplexes of **TCB** with sterically hindered alkylbenzenes are detectable in **TCE**, a nonaromatic solvent.

Figure 4 gives the kinetics curves of the fluorescence emission of **TCB**−**DUR** and **TCB**−**TIPB** exciplex systems. It has been reported that the decay times of these exciplexes exhibit a donor concentration dependence[14] that is believed to be caused by species with a stoichiometric ratio different from 1:1. The flat-donor concentrations used in the measurements of fluorescence decays are 0.05 M or less to avoid such an effect. From Figure 4, it is clear that the rise time of the exciplex fluorescence of **TCB** with **DUR** is much shorter than that with **TIPB**. The decay of exciplexes of **TCB** with both **DUR** and **TIPB** can be described by a single exponential. The lifetimes for the decay processes are 17.1 and 34.4 ns, respectively. Similarly, the lifetimes of exciplexes of **TCB** with other bulky donors and their matched flat donors are measured in **BEN**, **TOL**, and other solvents. The results are collected in Table 1. The lifetimes of the exciplexes of **TCB** with bulky donors are longer than those for matched flat donors by a factor of 1.6 to 3.3. In other words, the decay rates of the former are slower than those of the latter by a factor of 1.6 to 3.3.

Exciplexes are intermediate species that commonly exist after electron-transfer quenching. To reach a clear understanding of their role in electron-transfer quenching, many systems and technologies have been explored since pioneering work by Weller and co-workers.[1] It is generally believed that there is strong electronic coupling between electron donor and acceptor molecules in exciplexes. The involvement of an exciplex is avoided when theory[2] is used to analyze the electron-transfer process of weakly coupled systems in solution.[16] The fluorescence quantum yield after charge-transfer quenching is determined by both the exciplex-formation yield at the encounter and the relative rate of nonradiative and radiative decay in the exciplex. In the mechanism proposed by Weller and co-workers,[3] it was assumed that the formation efficiency of exciplexes is the key factor in controlling fluorescence quantum yields after electron-transfer quenching. In the theory developed by Mataga et al.,[4] more attention is paid to the effect of the relative rates of radiative decay to nonradiative decay on the fluorescence quantum yield in solvents of different polarities. The electron donor−acceptor separation distance is a key factor that controls the formation efficiency and radiative and nonradiative decay rates of exciplexes. There have been earlier studies concerning steric effects in exciplex photophysics. Unfortunately, no emission could be observed when sterically bulky donors or acceptors were used in these studies.[5−8] According to Hubig et al., this results from a changeover from an inner-sphere mechanism with strong electronic coupling to an outer-sphere mechanism with weak electronic coupling in the photoinduced electron transfer. It is unlikely that bulky electron donor and acceptor systems with weak electronic coupling will form exciplex or exciplex-like encounter complexes even in nonpolar solvents. The results presented here indicate that the steric hindrance-induced weakness in electronic coupling might not be critical in controlling the formation of exciplexes. To get a better understanding of the interaction between donor and acceptor molecules, the compositions and structures of the exciplexes between **TCB** and bulky donors need to be elucidated. The contributions of the electronic coupling and Franck−Condon factor in the steric hindrance-induced decrease in the decay rate also need to be separated.

3.2. Deuterium Isotope Effects. Deuterium isotope effects in return electron-transfer processes have been explored under different conditions.[17−19] The occurrence of an isotope effect in the nonradiative return electron-transfer rate indicates the contribution of vibrations involving the substituted atoms to the Franck−Condon envelope of the electronic transition.[17,18] For **EDA** systems between methyl-substituted benzene donors and various acceptor molecules, it was found that there exists a significant decrease in return electron-transfer rates upon deuterium substitution of the methyl hydrogens of the donors, but the effect of deuterium substitution of the ring hydrogens on the return electron-transfer rate is less significant.[17,18] This is understood from the point of view that there is a strong coupling of stretching vibrations involving the methyl hydrogen via a hyperconjugative mechanism for the return electron-transfer process.

In the present study, the experiments are conducted in **BEN**, **TOL**, and **PXY**. These solvents by themselves are electron donors. When a stronger donor is added to the solution, the fluorescence of exciplexes of **TCB** with these solvent molecules is quenched, and a new emission band at lower energy appears. It is unclear whether the new emission is caused by a 1:1 exciplex of **TCB** with the added donor and without the active involvement of the solvent molecule in the exciplex structure or the new emission is from a three component exciplex ($\mathbf{AD_2D_1}$ or $\mathbf{D_1AD_2}$) with both the added donor and solvent molecule contained in the structure. We use the deuterium isotope effect to probe the involvement of solvent molecules in the exciplex after electron-transfer quenching. Figure 5a compares the steady-state emission spectra of $\mathbf{TOL\text{-}h_8/TCB}$ and $\mathbf{TOL\text{-}d_8/TCB}$ after excitation at 355 nm in pure solvents $\mathbf{TOL\text{-}h_8}$ and $\mathbf{TOL\text{-}d_8}$, respectively. Perdeuteration has no significant effect on either the position or band shape of the exciplex emission. However, the intensity for the $\mathbf{TOL\text{-}d_8}$ exciplex is about 2.1 times as large as that for the $\mathbf{TOL\text{-}h_8}$ exciplex. The emission decays detected at 580 nm for $\mathbf{TOL\text{-}h_8/TCB}$ and $\mathbf{TOL\text{-}d_8/TCB}$ after excitation at 355 nm are shown in Figure 5b. The decays are single-exponential. The fluorescence lifetimes of the $\mathbf{TOL\text{-}h_8}$ and $\mathbf{TOL\text{-}d_8}$ exciplexes are 73 and 174 ns, respectively. The fluorescence lifetime increases by a factor of 2.3, which is in

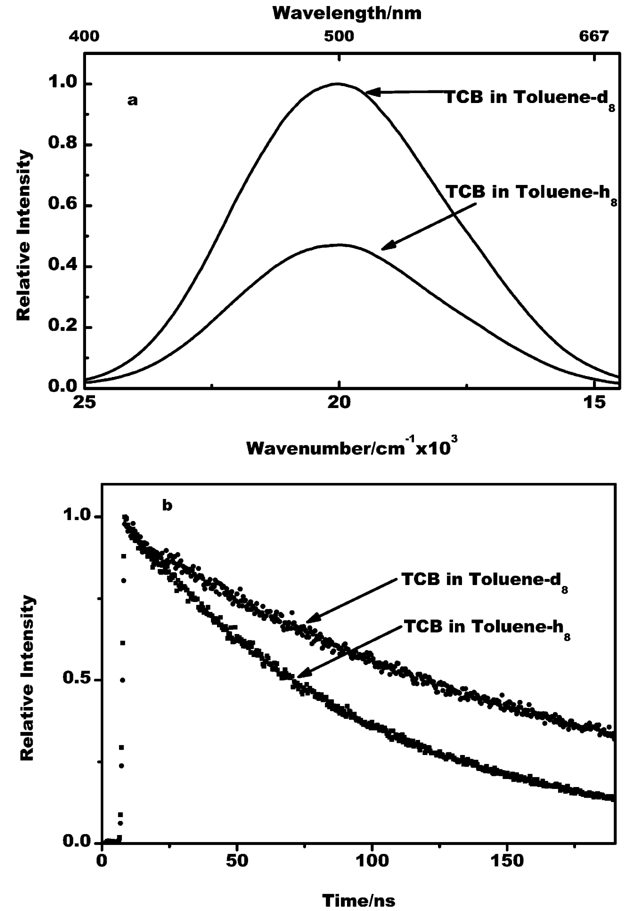


Figure 5. (a) Steady-state emission spectra and relative intensities of **TCB** in **TOL-h$_8$** and **TOL-d$_8$**. (b) Decay curves of the **TCB** exciplex of **TOL** in **TOL-h$_8$** and **TOL-d$_8$**.

reasonable agreement with the perdeuteration-induced increase in the steady-state fluorescence intensity. From **BEN-h$_6$/TCB** to **BEN-d$_6$/TCB**, perdeuteration-induced increases in the fluorescence lifetime and relative intensity by factors of 1.4 and 1.5, respectively, are observed. For the present systems, the quantum yields of the fluorescence emission are low. The changes in the fluorescence lifetime and relative intensity can be attributed to the changes in the nonradiative return electron-transfer rate. As discussed in section 3.1, when **DUR** or **TIPB** at low concentration ($<$0.05 M) is added to a **TOL** solution of **TCB**, the exciplex between **TOL** and **TCB** formed after excitation at 355 nm is quenched, and a new exciplex with an emission maximum at 544 (**DUR**) or 554 nm (**TIPB**) appears. We expect that a significant deuterium isotope effect of the **TOL** solvent should be observed in the fluorescence lifetime and relative intensity if **TOL** is actively involved in the structure of the exciplex formed after electron-transfer quenching. Figure 6 shows the fluorescence rise and decay curves of **DUR/TCB** in **TOL** and **TOL-d$_8$** and of **TIPB/TCB** in **TOL-h$_8$** and **TOL-d$_8$**. The fluorescence decay curves of both **DUR/TCB** and **TIPB/TCB** exhibit no detectable change following the perdeuteration of the **TOL** solvent. The rise time for **TIPB/TCB** in **TOL-d$_8$** is longer than that in **TOL-h$_8$**, which means that the exciplex formation of **TIPB/TCB** is slower in **TOL-d$_8$** than that in **TOL-h$_8$**. This is because the rate of electron-transfer quenching by **TIPB** for the **TOL-d$_8$/TCB** exciplex is slower than that for the **TOL-h$_8$/TCB** exciplex. When **BEN** or **PXY** is used as the solvent, similar results are obtained. This implies that the exciplex formed after quenching can be approximately described as a two-component system between the second stronger donor added and **TCB**. The role of **TOL**, **BEN**, and **PXY** is to serve as a solvent without significant involvement in the exciplex structure.

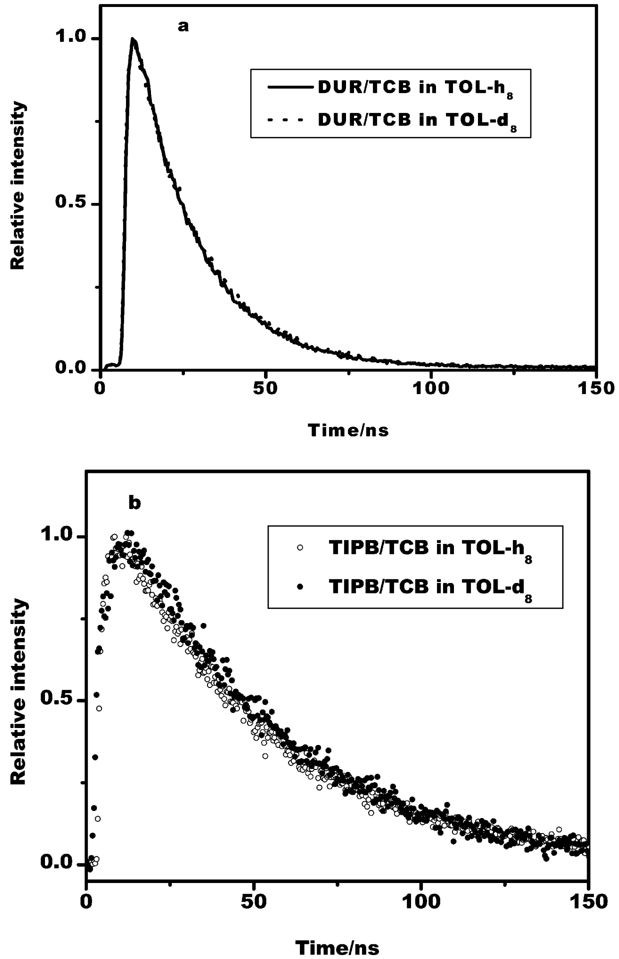


Figure 6. (a) Decay curves of the **TCB−DUR** complex in **TOL-h$_8$** and **TOL-d$_8$**. (b) Decay curves of the **TCB−TIPB** complex in **TOL-h$_8$** and **TOL-d$_8$**.

3.3. Effect of Driving Force and Separation Distance on the Recombination Rate. The exciplex decays by one of the following four paths (Scheme 2): radiative (k_f) and nonradiative return electron transfer (k_{-et}), which will reform the ground -state complexes, intersystem crossing to the locally excited triplet state (k_{isc}), and separation into **SSRIP**s. Intersystem crossing and **SSRIP** formation are unlikely in the present system because the energies of both ^{3}**A*** and ^{3}**D*** are above that of the exciplexes studied here[12,17] and Coulombic interactions within the exciplex are strong in the nonpolar solvents used, preventing the transformation from exciplexes to **SSRIP**s.

The measured decay rate constant is the sum of the rate constants of the return electron transfer of both radiative and nonradiative decays. The rate constant of radiative return electron transfer is given by[12]

$$k_f = \frac{64\pi^4}{3h^3c^3} n^3 \nu_{av} H_{ab}^2 \Delta\mu^2 \tag{1}$$

where n is the solvent refractive index, c is the speed of light, k_f is the emission rate constant at frequency ν, and $\Delta\mu$ is the magnitude of the difference in the static dipole moment of the neutral (**DA**) and exciplexes (**D**$^{+\delta}$**A**$^{-\delta}$). ν_{av} is the average emission frequency of **CRIP**s. k_{-et} can be calculated from the driving force ($-\Delta G°_{-et}$), solvent (λ_s), and intramolecular (λ_v)

reorganization energy terms. The calculation of the nonradiative rate constant of return electron transfer involves the product of the square of the electronic coupling element, $H_{ab}{}^2$, and a Franck−Condon term, $\mathrm{FC}(\Delta G^\circ{}_{-et})$:[20]

$$k_{-et} = \frac{2\pi}{\hbar} H_{ab}{}^2 \mathrm{FC}(\Delta G^\circ{}_{-et}) \tag{2a}$$

$$H_{ab}{}^2 = H^\circ{}_{ab}{}^2 \exp[-\beta(r - r_0)] \tag{2b}$$

$$\mathrm{FC}(\Delta G^\circ{}_{-et}) = (4\pi\lambda s k_B T)^{-1/2} \sum_{n=0}^{\infty} \frac{e^{-S} S^n}{n!} \exp\left(-\frac{(\Delta G^\circ{}_{-et} + \lambda s + nh\nu)^2}{4\lambda_s k_B T}\right) \tag{2c}$$

$$S = \frac{\lambda_v}{h\nu} \tag{2d}$$

The electronic coupling element, H_{ab}, is assumed to decrease exponentially with increasing separation distance r (eq 2b), and $H^\circ{}_{ab}$ is the value of H_{ab} at the contact separation distance r_0. The β factor measures the decrease in electronic coupling with donor/acceptor separation distance. In eq 2c, k_B is Boltzmann's constant. The Franck−Condon term is a function of the driving force ($-\Delta G^\circ{}_{-et}$), the solvent reorganization energy (λ_s), and a reorganization energy (λ_v) associated with a representative averaged high-frequency model (ν). The driving force ($-\Delta G^\circ{}_{-et}$) and the solvent reorganization energy (λ_s) are calculated by eqs 3 and 4, respectively.

$$\Delta G_{-et}{}^\circ = E_{1/2}{}^{red} - E_{1/2}{}^{ox} + \frac{e^2}{\epsilon_s r} \tag{3}$$

$$\lambda_s = e^2\left(\frac{1}{2r_D} + \frac{1}{2r_A} - \frac{1}{r}\right)\left(\frac{1}{\epsilon_{op}} - \frac{1}{\epsilon_s}\right) \tag{4}$$

$E_{1/2}{}^{red}$ is the reduction potential of **A**, $E_{1/2}{}^{ox}$ is the oxidation potential of **D**, and $e^2/(\epsilon_s r)$ is the Coulomb attraction energy for the exciplex (or geminate radical ion pair) at separation distance r where return electron transfer takes place. ϵ_{op} and ϵ_s are the optical and static solvent dielectric constants, respectively.

For the present systems, quantum yields for radiative return electron transfer (Φ_r) are less than 1% for most of the **D/A** pairs, thus the decay rate constants reflect nonradiative return electron transfer. Φ_r can be estimated from the combination of eqs 1 and 4 as

$$\Phi_r = \frac{k_f}{k_{-et}} = \frac{\dfrac{64\pi^4}{3h^3c^3} n^3 \nu_{av} H_{ab}{}^2 \Delta\mu^2}{\dfrac{4\pi^2}{h} H_{ab}{}^2 \mathrm{FC}(\Delta G_{-et})} = \frac{16\pi^2 n^3 \nu_{av} \Delta\mu^2}{3h^2c^3 \mathrm{FC}(\Delta G_{-et})} \tag{5}$$

Equation 5 indicates that, in a given solvent, Φ_r is mainly determined by $\Delta\mu$ and the Franck−Condon factor but is independent of the electronic coupling term that affects both the radiative and nonradiative return electron transfer in the same way. For exciplexes of donor−acceptor pairs of bulky and flat donors with similar structures and electron-transfer properties, the **D/A** separation distances with bulky donors are about 1.1 Å larger than those with flat donors. This significantly increases the $\Delta\mu^2$ term and makes a favorable contribution to radiative return electron transfer. However, as expected from eqs 3 and 5, the increased separation distance will result in a decreased driving force, which increases the rate of nonradiative return electron transfer because all of the return electron-transfer processes in the present study are located in the Marcus "inverted region".

From Table 1, it can be noted that the relative emission intensities of exciplexes of bulky donors to the matched flat donors (I_{SH}/I_{SUH}) are around 1; that is, steric effects have almost no influence on fluorescence quantum yields of the exciplex. This means that steric hindrance decreases both radiative and nonradiative decay in about the same way. As a result, fluorescence yields remain more or less constant. In other words, the increased radiative decay rate caused by the steric hindrance-induced increase in the $\Delta\mu^2$ term is balanced by the increased nonradiative decay rate caused by an increase in the Franck−Condon term.[21] Because we do not have clear evidence that the steric hindrance-induced increase in the $\Delta\mu^2$ term is independent of the electron donation properties of the donor molecules, the steric hindrance effect on emission quantum yields of exciplexes cannot be used to probe the steric hindrance-induced change in the Franck−Condon term in a quantitative way. A general assumption in treating the nonradiative decay as a return electron-transfer process is that charge separation is complete in these excited **EDA** pairs. This is not true for **EDA** pairs of weak electron acceptors with alkylbenzene donors in nonpolar solvents. Comparing the electronic properties of the donor and acceptor molecules used in this work with those in the literatures,[20,22] we find that the exciplexes here are better described as partially charge-separated **EDA** pairs than as complete charge-separated ion pairs. The exciplexes of **TCB** with strong donors such as **DUR** and **HMB** and their matched bulky molecules are expected to exhibit a higher degree of charge separation than do those with weak donors such as **BEN**, **TOL**, **PXY**, **MS**, and the related matched sterically hindered ones. The steric hindrance-induced increase in the $\Delta\mu^2$ term should be larger for strong donors than for weak donors. The fact that I_{SH}/I_{SUH} is almost independent of the electronic properties of donor molecules might imply that a steric hindrance-induced increase in the Franck−Condon term[21] is also larger for strong donors than for weak donors. This is understandable because, as will be discussed later, the reorganizational terms of the exciplexes of **TCB** with substituted benzenes decrease as the donor strength increases.[12] From eq 4, we see that the decreased reorganizational energy of a strong donor will make the Franck−Condon term more sensitive to the steric hindrance-induced decrease in the driving force.

Moreover, results from several investigations indicate that rate constants of exciplexes or excited **EDA** complexes exhibit a linear driving force dependence. This is not predicted by nonadiabatic electron-transfer theory.[12,23,24] To interpret such a discrepancy, Gould et al argued that, on the basis of their fluorescence spectral fitting, there exists a decreased solvent reorganization energy with an increasing number of methyl groups on donor molecules.[12,25] Alternatively, Hubig et al.[10] proposed that these return electron transfers are inner-sphere processes in nature and cannot be described using nonadiabatic ET theory. The inner-sphere character of these strongly coupled species (>1000 cm $^{-1}$) is demonstrated by their high sensitivity to steric effects. As shown by Hubig et al and others, exciplexes or exciplex-like encounter complexes are generally undetectable if a bulky donor or acceptor molecule is used.[9,10] They argue that there is a sterically controlled changeover from an inner-sphere to an outer-sphere mechanism. Our results indicate that this is not so. Because exciplexes of **TCB** with bulky donors and their matched flat donors have about the same driving force, we expect that the present system can provide us with insights

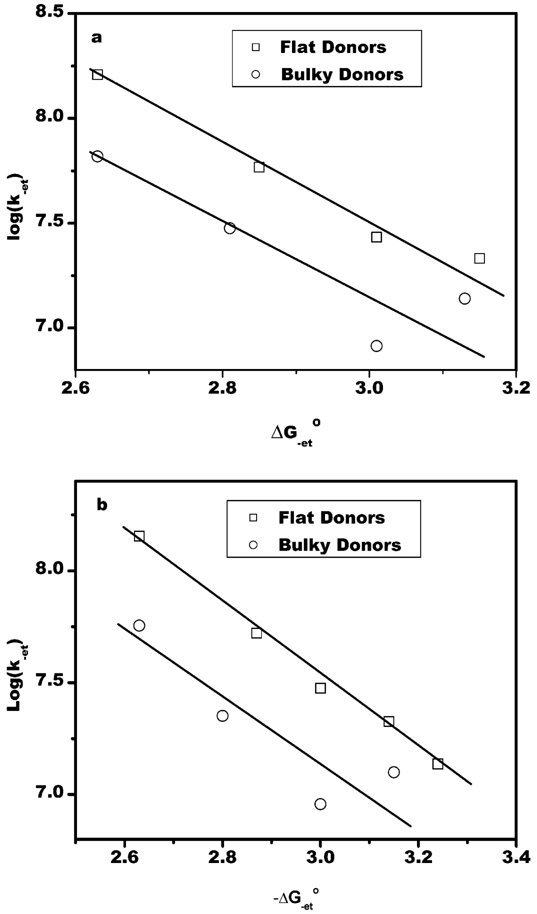


Figure 7. (a) log($k_{-\mathrm{et}}$) vs driving force, $-\Delta G_{-\mathrm{et}}{}^{\circ}$, in **BEN** for **TCB** exciplexes of flat and bulky donors. (b) log($k_{-\mathrm{et}}$) vs driving force, $-\Delta G_{-\mathrm{et}}{}^{\circ}$, in **TOL** for **TCB** exciplexes of flat and bulky donors.

into the dependence of rate constants of return electron transfers on the driving force at different separation distances.

As discussed above, the contributions of intersystem crossing, free-ion formation, and radiative decay are small and can be ignored for the present systems. The rate constants of nonradiative return electron transfer can be calculated directly from the lifetime data listed in Table 1. When log($k_{-\mathrm{et}}$) values of **TCB** with flat and bulky donors in **BEN** and **TOL** are plotted against the driving force, $-\Delta G^{\circ}_{-\mathrm{et}}$ (Figure 7 a and b), both exhibit near-linearity with a slope around −1.4. The slope value is similar to that previously reported. $-\Delta G^{\circ}_{-\mathrm{et}}$ values used in the plots are obtained by fitting the emission profiles using eqs 2a−2d.[12] A typical ν_v value of 1400 cm^{-1} is used in the fitting. When bulky donors are used, a decrease in the nonradiative return electron-transfer rate by a factor of 1.6−3.3 is observed. As we have discussed, when the separation is increased, the Franck−Condon term makes a favorable contribution to increase the return electron-transfer rate. This suggests that the observed steric-induced decrease in the return electron-transfer rate is caused by the decreased electronic coupling strength between donor and acceptor molecules. The similarity in the driving force dependence of nonradiative rate constants of exciplexes with both flat and bulky donors implies that the separation distance (the strength of electronic interaction) between donor and acceptor molecules in exciplexes has only a limited effect on the driving force dependence. No clear changeover from an inner-sphere to an outer-sphere mechanism exists in the present systems.

When the Marcus equation is used to treat weakly coupled electron-transfer systems, a bell-shaped plot of the logarithm of the rate constant for electron transfer against the driving force for the reaction is usually obtained. The precondition for using the Marcus equation correctly to predict the relationship between the rate constant and the driving force is that the concerned systems have similar reorganizational terms but different driving forces. The reorganizational term can be estimated from the Stokes shift:[26]

$$2\lambda = \nu_{\mathrm{a}}^{\max} - \nu_{\mathrm{f}}^{\max} \tag{6}$$

From Figure 1 and Table 1, the Stokes shifts for exciplexes of **TCB** with **BEN**, **TOL**, **PXY**, **MS**, **DUR**, and **HMB** are determined to be 12, 12, 11, 9.1, 9.2, and 7.9 kcm^{-1}, respectively. The results indicate that the reorganizational term shows a significant decrease as the number of methyl groups on the donor molecules increases. This will in turn have a notable impact on the driving force dependence of the rate constant of the nonradiative return electron-transfer process.

4. Conclusions

The formation of radiative exciplexes of a series of electron donor−acceptor pairs of 1,2,4,5-tetracyanobenzene (**TCB**) and bulky alkyl-substituted benzenes is reported for the first time in nonpolar solvents **BEN**, **TOL**, and **PXY**. The dependence of radiative and nonradiative electron transfer on the driving force and separation distance in the radical ion pairs is explored. It is found that exciplexes of donor−acceptor pairs of bulky and flat donors with similar structures and electron-transfer properties give almost the same fluorescence quantum yields. Nonradiative return electron-transfer rate constants of exciplexes of **TCB** with both sterically unhindered and hindered donors are determined by single-photon timing; the rate constants of exciplexes with bulky donors are 1.6−3.3 times smaller than those with matched flat donors. The solvents that are used are donors by themselves. To test their involvement in the structures of exciplexes after electron-transfer quenching by added strong donor molecules, deuterium isotope effects on the exciplexes were studied. Isotope effects on return electron-transfer rate constants of the exciplexes described above are found to be undetectable. This implies that the exciplexes that are formed are two-component systems without the structural involvement of a solvent. Nearly-linear relationships between nonradiative electron-transfer rate constants, log($k_{-\mathrm{et}}$), and the driving force, $-\Delta G^{\circ}_{-\mathrm{et}}$, are observed for exciplexes from both sterically unhindered and sterically hindered donors. This indicates that for the present systems there is no sterically controlled changeover from inner-sphere to outer-sphere mechanisms as suggested by Hubig et al.[10]

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